Water Assisted Growth of Two-Dimensional MoS₂/MoSe₂ Vertical Heterostructures on Molten Glass

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Experimental Section

1. CVD Synthesis of MoS₂ Monolayers

A two-zone CVD horizontal quartz tube furnace was employed to grow MoS₂ monolayers. Sulfur powder (320 mg) was placed in upstream zone 1. The Mo foil was ultrasonically cleaned in acetone, ethanol, and water for 15 min, respectively. The pretreated Mo foil was placed above the soda-lime glass substrate in a parallel geometry with a gap of 6 mm in the downstream zone 2. Before heating, 400 sccm Ar was flowed into the tube for 15 min to ensure a stable chemical reaction environment. Then the flow rate of Ar was controlled at 30 sccm for the following process. The temperature of zone 1 and zone 2 were heated to 200 °C and 720 °C in 35 min, respectively, and kept at that temperature for 4 min under an argon atmosphere. Herein, water vapor was introduced into the furnace by Ar carrier gas to synthesize large scale uniform MoS₂ Monolayers.

2. CVD Synthesis of vertical MoS₂/MoSe₂ heterostructure

The $MoS_2/MoSe_2$ vdW heterostructures were fabricated using a sequential CVD method similar to the growth of MoS_2 Monolayers. The proper ratio of S (320 mg) and Se (90 mg) mixture powder are put in the upstream zone 1. The pretreated Mo foil was placed faced down on the soda-lime glass substrate in a parallel geometry with a gap of 6 mm in the downstream zone 2. Before heating, 400 sccm Ar was flowed into the tube for 15 min to ensure a stable chemical reaction environment. Then the flow rate of

Ar was controlled at 30 sccm for the following process. The temperature of the zone 1 was heated to 200 °C in 35 min and kept at this temperature for 4 minutes for the growth of MoS₂ monolayers. Then the temperature quickly heated to 250°C in 4 min and keep for 4min for Se evaporation. The temperature of zone 2 was heated to 750 °C in 35 min and kept at this temperature for 12 minutes. After growth, the furnace was rapidly cooled to 400 °C to prevent additional reactions and then cooled down to room temperature. Eventually, epitaxially grown vertical MoS₂/MoSe₂ vdW heterostructures were obtained on the glass substrate.

3. Methods for sample transferring.

The synthesized $MoSe_2/MoS_2$ heterostructures can be transferred onto any substrates (SiO₂ /Si or soft substrate) using a modified poly(methyl methacrylate) (PMMA)-based wet transfer method. The $MoS_2/MoSe_2$ heterostructures substrate was spin-coated with PMMA and was baked at 120 \Box C for 3 min. Then makes cracks along the edge of PMMA/MoSe₂/MoS₂ with a knife. Subsequently, the PMMA/MoSe₂/MoS₂ film will delaminate from the glass substrate after injecting water due to their different surface energies. Floating PMMA/sample films in water were scooped with the target substrates. We then immersed the substrates in acetone to remove PMMA films.

4. Structure and Composition Characterization

Optical images of the $MoSe_2/MoS_2$ heterostructures were taken on an optical microscopy (Nikon, LV150N). Atomic force microscopy (AFM) images were acquired with a Bruker Dimension Icon operating in ScanAsyst mode using Bruker ScanAsyst-Air probes (silicon tip; silicon nitride cantilever, spring constant: 0.4 N·m⁻¹, frequency: 70 KHz). The images were analyzed using NanoScope Analyst software (version 1.40). Raman and PL measurements were performed on Invia Reflex micro-Raman spectroscope with 532 nm laser at room temperature. Raman spectra were calibrated by the Raman shift of single-crystal silicon at 520.4 cm⁻¹. Raman measurements were conducted using an 1800 g/mm grating to disperse the signal and generate a spectral resolution of less than 1 cm⁻¹ (a 600 g/mm grating was used for PL measurements).

5. Methods for TEM Characterizations

For the TEM specimen preparations, we transferred the synthesized MoSe₂/MoS₂ heterostructures onto Cu grids using a modified poly(methyl methacrylate) (PMMA)-based wet transfer method. The MoSe₂/MoS₂ heterostructures substrate was spin-coated with PMMA and was baked at 120 °C for 3 min. Then makes cracks along the edge of PMMA/ MoSe₂/MoS₂ with a knife. Subsequently, the PMMA/ MoSe₂/MoS₂ film will delaminate from the glass substrate after injecting water due to their different surface energies. Floating PMMA/sample films in water were scooped with a TEM grid (Holey carbon coated with 400-meshed Cu). We then immersed the grids in acetone to remove PMMA films. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning-TEM (STEM) imaging were performed with FEI Tecnai F20 microscope with an accelerating voltage of 200 kV. For the SHG measurements, a mode-locked Ti:sapphire laser (Tsunami HP) centered at 800 nm (\approx 100 fs, 80 MHz) was amplified by a regenerative amplifier system (Spitfire Ace-PA-100, 1 kHz). And the resulting signal was collected by the above Raman system with a 100× objective. For the polarization-dependent SHG measurements, the signal was recorded every 10° of rotation of the sample in all 360° angles.

6. Fabrications and Measurement of the MoS₂/MoSe₂ Devices

For the device fabrication, the $MoSe_2/MoS_2$ vdW heterostructures are first transferred to a SiO₂ (300 nm)/Si substrate. Then, a layer of MMA copolymer was spin-coated on the TMDs heterostructures, followed by a 1 min bake at 160 °C on the hot plate. After this, another layer of PMMA was spin-coated on the substrate followed by a 5 min bake at 160 °C. Electron beam lithography was employed to define the drain and source electrodes by an 80 seconds XeF₂ etching. After the conventional development process, Ti/Au metal layer (10 nm/100 nm) was deposited to form the source-drain electrodes by electron beam evaporation and finally followed by a lift-off process with acetone. All of the devices are annealed at 5×10^{-6} mbar, 420 K for 2 hours to reduce contact resistance and remove absorbed moisture. The electrical and optoelectronic properties of the heterostructures were measured in a vacuum with the Lake Shore Probe Station and Keithley 4200 semiconductor analyzer at room temperature.

7. Calculation of carrier mobility

For the calculation of carrier mobility, the method used is to measure the leakage current in the linear region at low V_{ds} . Then according to the following formula,

$$\mu = \frac{g_m}{C_{ox}V_{ds}} \cdot \frac{L}{W}$$

$$g_m = \frac{\partial I_{ds}}{\partial V}$$

where UV_{gs} , which is the slope of the linear region of the I_{ds} - V_{gs} curve; V_{ds} is the drain voltage;

 $C_{\text{ox}} = \frac{\varepsilon_0 \varepsilon_{r1}}{d_{ox}} \quad \text{, where } \varepsilon_0 = 8.85 \times 10^{-12} F m^{-1} = \varepsilon_{r1} = 3.9 \text{, and } d_{ox} (SiO_2) = 90 nm; \text{ and } L \text{ and } W$

are the length and width of the channel, respectively.

8. DFT Calculation Details

DFT calculations have been carried out in AtomistixToolKit (ATK) 2019.0 with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation within the generalized gradient approximation (GGA). We employ a $5 \times 5 \times 1$ Monkhorst-Pack k-point grid with the cutoff energy of 50 Hartree. A repeating sheet model consisting of a 4×4 lateral periodicity of TMDs was used.

Supplementary Figures



Figure S1. (a) XRD patterns of Mo foils after CVD process with and without the assistance of H₂O.



Figure S2. OM images of the as-prepared MoS_2 crystals on glass substrate with different Ar/water vapor flow rate. (a) 10 sccm,(b) 30 sccm, (c) 50 sccm, (d) 70 sccm.

Different Ar/water vapor flow rate of, 30sccm, 50sccm, and 70sccm was injected into the furnace as shown in **Figure S2**. In a mild H₂O concentration (mild oxidization of the Mo foil), the size of MoS₂ increased as the increasing concentration of H₂O from 10 to 30 sccm, which is due to the gradually increased oxidization of the Mo foil and sufficient supply of the MoO_x precursor. When excess H₂O is introduced into the furnace (flow rate >50 sccm), the etching effect will be occurred on MoS₂ (Figure S2c), eventually leading to the formation of cracked samples (Figure S2d).



Figure S3. OM images of the as-prepared MoS_2 crystals on glass substrate with different gap distance between the Mo foil and the glass substrate . (a) 10 mm, (b) 8 mm, (c) 6 mm, (d) 2 mm.

The large gap distance between the Mo foil and the glass substrate lead to high sulfur concentration over the gap region. It can be seen that plenty of triangular MoS_2 is formed on glass substrate with the gap of 10 mm (**Figure S3a**), the small size of products is due to the high sulfur concentration and high nucleation density. When the gap is decreased from 10 to 6 mm (**Figure S3a-c**), the gradual reduction in sulfur concentration over the gap region is happened, which suppressed the nucleation density and increases the size accordingly. However, when the gap is further reduced to 2 mm (**Figure S3d**), irregularly shaped crystals formed due to the insufficient feeding of the S precursor, similar to the published report (*Nat. commun. 2018, 9, 979.*).



Figure S4. (a) OM images of the as-prepared MoS₂/MoSe₂ heterostructures on glass substrate. **(b)** OM images of the as-prepared MoSe₂/MoS₂ heterostructures on SiO₂/Si substrate. **(c)** SEM image of the as-prepared MoSe₂/MoS₂ heterostructures on SiO₂/Si substrate.



Figure S5. OM images of six representative $MoSe_2/MoS_2$ heterostructures with different Se reaction time of (a) 0 min, (b) 3 min, (c) 4 min, (d) 5 min, (e) 6 min and (f) 7 min, respectively. Scale bar: 5µm.



Figure S6. (a) OM image of the prepared MoS₂/MoSe₂ heterostructure on glass substrate with excess Se precusor. **(b)** SEM image of the prepared MoS₂/MoSe₂ heterostructure on Si/SiO₂ substrate with excess Se precusor.



Figure S7. Energy Dispersion Spectroscopy (EDS) of heterostructure collected from the MoS_2 monolayer (a) and $MoSe_2/MoS_2$ bilayer (b), respectively. The EDX spectrum for MoS_2 monolayer (**Figure S7a**) revealed that only the existence of Mo and S elements with the Mo:S atomic ratio of 1:2, and there are no Se signal can be detected. Besides, the EDX spectrum collected from $MoSe_2/MoS_2$ bilayer (**Figure S7b**) presents the atomic ratio of Se:S is 1:1. The element analysis results further demonstrated that both the MoS_2 and $MoSe_2$ is pure phase without S or Se doped.



Figure S8. (a) The schematic of MoS₂/MoSe₂ field-effect transistor (FET). multi-electrode backgate field-effect transistors (FETs). (b) The optical image of a typical MoSe₂/MoS₂ FETs. Electrodes E1, E2, E5 and E6 were deposited on the top of the stack MoSe₂/MoS₂, while E3 and E4 on top of the monolayer MoS2. Hence, three kinds of device channels were formed, (1) Monolayer MoS₂ channel (electrodes E1 and E2), (2) bilayer MoSe₂/MoS₂ channel (electrodes E5 and E6) and (3) bilayer MoSe₂/MoS₂-monolayer MoS₂ channel (electrodes E3 and E4), respectively. (c) Transfer characteristics of back-gated bilayer MoSe₂/MoS₂ FET and bilayer MoSe₂/MoS₂-monolayer MoS₂ FET.